Louis de Broglie (1892-1987) who was working on his Ph.D. degree at the time, made a daring hypothesis:

if radiant energy could, under appropriate circumstances behave as though it were a stream of particles, then could matter, under appropriate circumstances, exhibit wave-like properties?

For example, the electron in orbit around a nucleus.

DeBroglie suggested that the electron could be thought of *as a wave with a characteristic wavelength.*

He proposed that the wavelength of the electron was a function of its mass (m) and its velocity (ν) : $\lambda = \dfrac{h}{m^* \upsilon}$

i.e. the wavelength for "matter waves", where *h* is Planck's constant and is u velocity (not, the frequency). The quantity mu for any object is its *momentum* (mass * velocity).

What is the characteristic wavelength of an electron with a velocity of 5.97 x 10^6 m/s? (the mass of the electron is 9.11 x 10^{-28} g)

$$\lambda = \frac{h}{m^* \upsilon}$$

Planck's constant (h) is 6.63 x 10^{-34} J s (also, recall that 1J = 1 kg m^2/s^2)

$$\lambda = \frac{6.63 \text{ x } 10^{-34}\ \text{J s}}{(9.11 \text{ x } 10^{-28}\ \text{g}) * (5.97 \text{ x } 10^{6}\ \text{m s}^{-1})}$$

$$\lambda = 1.219 \text{ x } 10^{-13}\ \text{J s}^2\ \text{m}^{-1}\ \text{g}^{-1}$$

converting g to kg:

$$\lambda = 1.219 \text{ x } 10^{-13}\ \text{J s}^2\ \text{m}^{-1}\ \text{g}^{-1} * \left(\frac{1000g}{1Kg}\right) = 1.219 \text{ x } 10^{-10}\ \text{J s}^2\ \text{m}^{-1}\ \text{Kg}^{-1}$$

Converting from kg m^2/s^2 to Joules:

$$\lambda = 1.219 \text{ x } 10^{-10}\ \text{J s}^2\ \text{m}^{-1}\ \text{Kg}^{-1} * \left(\frac{1\ \text{Kg m}^2 / \text{s}^2}{1\ \text{J}}\right) = 1.219 \text{ x } 10^{-10}\ \text{m}$$

or 0.122 nm

- **The relationship between energy (*E*) and frequency (ν) for electromagnetic radiation (Planck's quantum of energy)**

$$E = h * \nu$$

- **The relationship between wavelength (λ) and frequency (ν) for electromagnetic radiation**

$$\lambda * \nu = c$$

From these relationships, we can determine the relationship between energy and wavelength:

$$E = h * \frac{c}{\lambda}$$

or, rearranging:

$$\lambda = h * \frac{c}{E}$$

- **The relationship between wavelength (λ) and momentum (m*v) for DeBroglie's "particle wave"**

$$\lambda = \frac{h}{\mathrm{m} * \mathrm{v}}$$

From the above relationships, we can calculate the relationship between energy (*E*) and momentum (m*v)

$$\frac{h}{\mathrm{m} * \mathrm{v}} = h * \frac{c}{E}$$

Simplify, and solve for *E* : $E = \mathrm{m} * \mathrm{v} * c$

The highest velocity (v) attainable by matter is the speed of light (*c*), therefore, the maximum energy would seem to be:

$$E = \mathrm{m} * c * c$$

or

$$E = \mathrm{m} * c^2$$

The Uncertainty Principle

For a relatively large solid object, like a bowling ball, we can determine its position and velocity at any given moment with a high degree of accuracy.

However, if an object (like an electron) has wave-like properties then how can we accurately define its' position?

Werner Heisenberg (1901-1976) concluded that due to the dual nature of matter (both particle and wavelike properties) it is impossible to simultaneously know both the position and momentum of an object as small as an electron.

Thus, it is not appropriate to imagine the electrons as moving in well-defined circular orbits about the nucleus.

Quantum Mechanics and Atomic Orbitals

1926 Erwin Schrödinger

***Schrödinger's wave equation* incorporates both wave- and particle-like behaviors for the electron.**

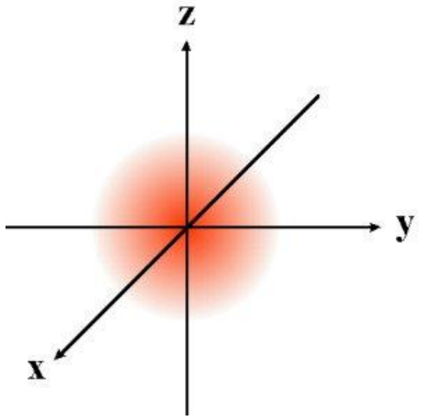
Opened a new way of thinking about sub-atomic particles, leading the area of study known as *wave mechanics*, or *quantum mechanics*.

Schrödinger's equation results in a series of so called wave functions, represented by the letter ψ *(psi)*. Although has no actual physical meaning, the value of ψ^2 describes the *probability distribution of an electron*.

From Heisenberg's uncertainty principle, we cannot know both the location and velocity of an electron. Thus, Schrödinger's equation does not tell us the exact location of the electron, rather it describes the *probability* that an electron will be at a certain location in the atom.

Departure from the Bohr model of the atom

In the Bohr model, the electron is in a *defined orbit*, in the Schrödinger model we can speak only of probability distributions for a given energy level of the electron. For example, an electron in the ground state in a Hydrogen atom would have a probability distribution which looks something like this (a more intense color indicates a greater value for ψ^2, a higher probability of finding the electron in this region, and consequently, greater electron density):



Orbitals and quantum numbers

Solving Schrödinger's equation for the hydrogen atom results in a series of wave functions (electron probability distributions) and associated energy levels. These wave functions are called *orbitals* and have a characteristic energy and shape (distribution).

The lowest energy orbital of the hydrogen atom has an energy of -2.18 x 10^{18} J and the shape in the above figure.

Note that in the *Bohr model* we had the same energy for the electron in the ground state, but that it was described as being in a defined *orbit*.

The Bohr model used a single quantum number (n) to describe an *orbit*, the Schrödinger model uses *three* quantum numbers: *n, l and m_l* to describe an *orbital*.

The principle quantum number 'n'

- **Has integral values of 1, 2, 3, etc.**
- **As n increases the electron density is further away from the nucleus**
- **As n increases the electron has a higher energy and is less tightly bound to the nucleus**

The azimuthal (second) quantum number 'l'

- **Has integral values from 0 to (n-1) for each value of n**
- **Instead of being listed as a numerical value, typically 'l' is referred to by a letter (*'s'=0, 'p'=1, 'd'=2, 'f'=3*)**
- **Defines the *shape* of the orbital**

The magnetic (third) quantum number 'm_l'

- **Has integral values between 'l' and -'l', including 0**
- **Describes the orientation of the orbital in space**

For example, the electron orbitals with a principle quantum number of 3 (i.e. *n*=3) would have the following available values of 'l' and 'm_l':

***n* (principle quantum number)**	***l* (azimuthal) (defines shape)**	***Subshell Designation***	**m_l *(magnetic) (defines orientation)***	***Number of Orbitals in Subshell***
3	**0**	**3s**	**0**	**1**
	1	**3p**	**-1,0,1**	**3**
	2	**3d**	**-2,-1,0,1,2**	**5**

- **A collection of orbitals with the same value of 'n' is called *an electron shell***
- **A collection of orbitals with the same value of 'n' and 'l' belong to the same *subshell***

Thus:

- **the *third electron shell* (i.e. 'n'=3) consists of the *3s, 3p* and *3d subshells* (each with a different shape)**
- **The *3s subshell* contains *1 orbital*, the *3p subshell contains 3 orbitals* and the *3d subshell* contains *5 orbitals*. (within each subshell, the different orbitals have different orientations in space)**
- **Thus, the *third electron shell* is comprised *of nine distinctly different orbitals*, although each orbital has the *same energy* (that associated with the third electron shell)**

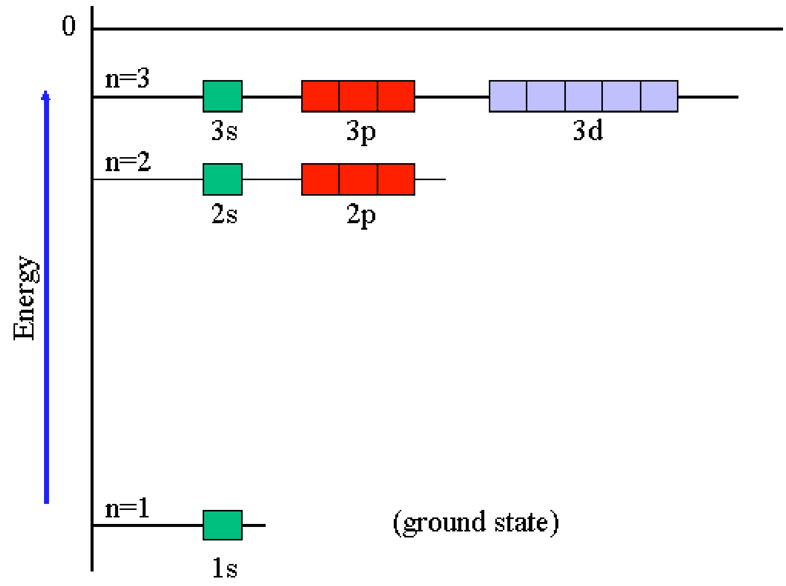
Note: remember, this is for hydrogen only.

Restrictions on the possible values for the different quantum numbers (n, l and m_l) gives rise to the following patterns for the different shells:

- **Each shell is divided into a number of *subshells equal to the principle quantum number* (e.g. the fourth shell is divided into four subshells: *s, p, d,*and *f*; whereas the first shell has a single subshell: *s*)**
- **Each subshell is divided into orbitals (*increasing by odd numbers*):**

Subshell	**Number of orbitals**
s	**1**
p	**3**
d	**5**
f	**7**

The number and relative energies of all hydrogen electron orbitals through n=3 are shown below:

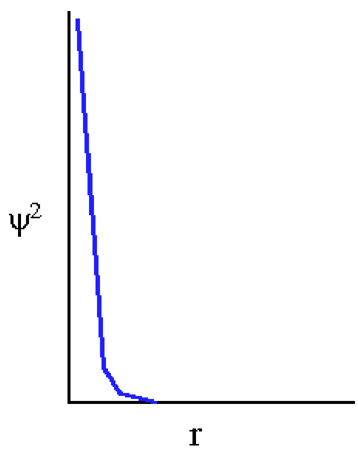


- **At ordinary temperatures essentially all hydrogen atoms are in their ground states**
- **The electron may be promoted to an excited state by the absorbtion of a photon with appropriate quantum of energy**

Representations of Orbitals

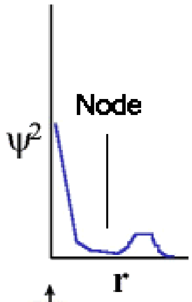
The *s* Orbitals

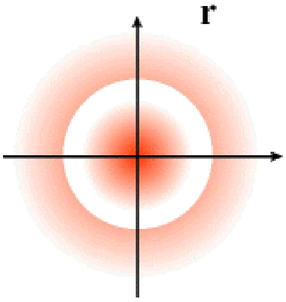
The *1s* orbital is spherically symmetrical. A plot of ψ^2 versus distance (r) from the nucleus shows a dramatic reduction in probability of finding the electron very far from the nucleus:



This indicates that in the ground state the electrostatic attraction of the electron for the proton in the nucleus is such that the electron is unlikely to be found far from the nucleus.

The higher energy s orbitals are also spherically symmetrical, however, they exhibit distinct nodes in the distribution probability:





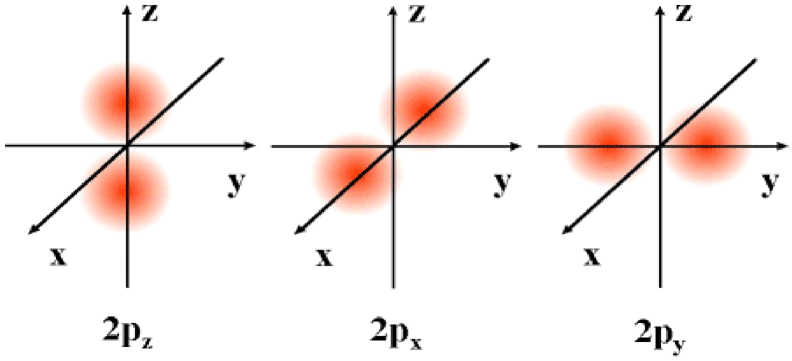
- **In the higher s orbitals there exists *node* regions where the electron density approaches zero (2s has 1 node, 3s has 2 nodes, etc)**
- **The higher s orbitals (excited states) have electron density distributions which indicate that there is a higher probability of finding the electron further away from the nucleus**

The size of the orbital increases as n increases

The most widely used representation of the Schrödinger orbits is to draw a boundary which represents 90% of the total electron density distribution. *For the s orbitals this would be a sphere representation*.

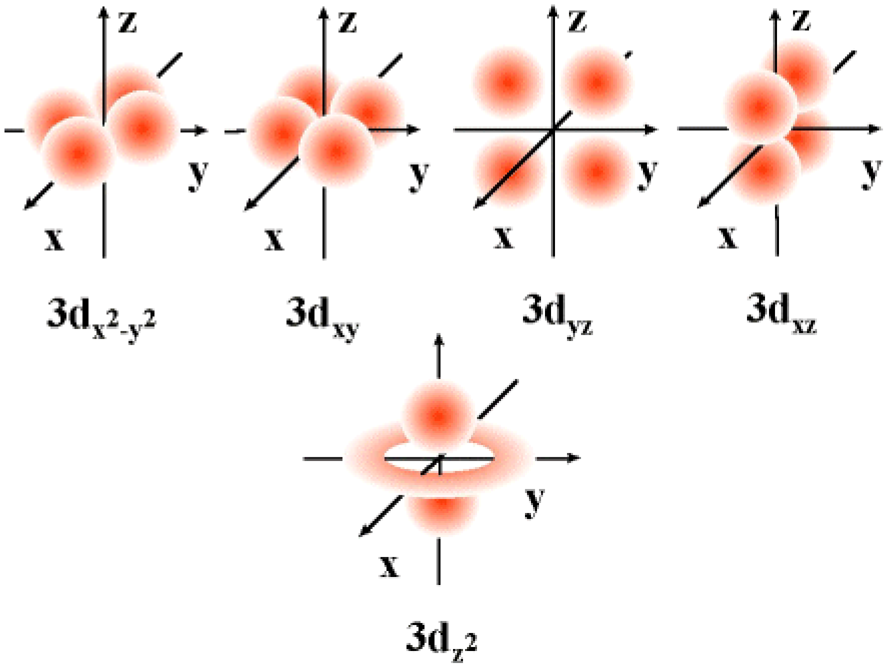
<u>*p* Orbitals</u>

- **The *p* orbitals are 'dumbbell' shaped orbitals of electron density, with a node at the nucleus.**
- **There are three distinct p orbitals, they differ in their orientations**
- **There is no fixed correlation between the three orientations and the three magnetic quantum numbers (m_l)**



<u>The *d and f* orbitals</u>

In the third shell and beyond there are five d orbitals, each has a different orientation in space:



Although the $3d_z2$ orbital looks different, it has the same energy as the other *d* orbitals.

There are 7 equivalent *f* orbitals (for each value of *n* 4 or greater). They are pretty difficult to represent on a 3-d contour diagram.

Understanding orbital shapes is key to understanding the molecules formed by combining atoms

<u>Orbitals in many-electron atoms</u>

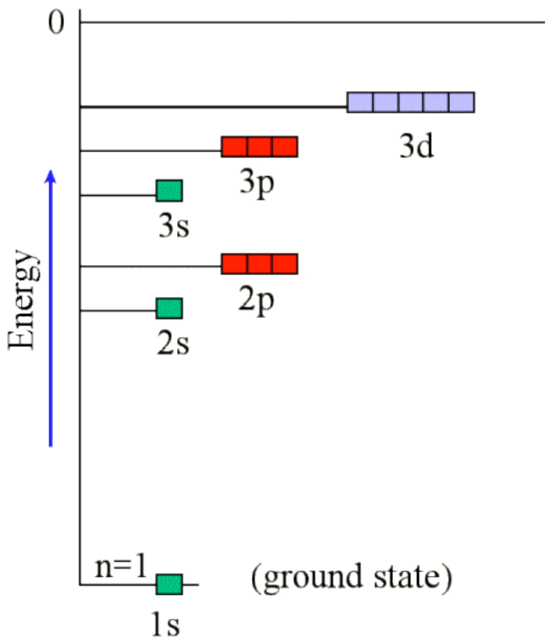
The hydrogen atom is a simple system having only *one electron*.

The quantum mechanical description of the hydrogen atoms places all subshells (i.e. *l* quantum number, or the *s, p, d* and *f* subshells) with the same principle quantum number (*n*) on the same energetic level.

An atom with more than 1 electron is called a *many-electron* atom.

Although the *shape* of electronic orbitals for many-electron atoms are the *same* as those for the hydrogen atom, *the presence of more than 1 electron influences the energy levels of the orbitals (due to electron-electron replusion)*.

For example, the 2s orbital is a lower energy state than the 2p orbital in a many-electron atom: (note: this is a qualitative representation for an "average" many-electron atom)



Effective Nuclear Charge

In a many-electron atom, each electron is simultaneously:

- ***attracted* to the protons in the nucleus**
- ***repelled* by other electrons (like-charge repulsion)**

What is the *average environment,* created by the nucleus and all the other electrons in the atom, which is "felt" by a particular electron in the atom?

The net positive charge attracting the electron is called *the effective nuclear charge*

- **Any electron density between the nucleus and the electron of interest will reduce the nuclear charge acting on that electron**
- **The effective nuclear charge (Z_{eff}) equals the number of protons in the nucleus (Z), minus the average number of electrons (S) that are between the electron in question and the nucleus**

$$Z_{eff} = Z - S$$

- **The positive charge "felt" by the outer electrons is *always less than the full nuclear charge* (inner electrons "screen" the nuclear charge).**

Energies of orbitals

The extent to which an electron will be screened by the other electrons depends on the shape of the electron distribution as we move out from the nucleus

- **Probability of being closer to the nucleus (based on orbital shapes) is as follows:**

$$(n)s < (n)p < (n)d < (n)f$$

closer further away

- **For the 3rd principle quantum number, for example, the 3*s* electrons experience the *least shielding* and the 3*d* electrons *the most***
- **Conversely, the 3*s* electrons experience a *greater* Z_{eff} and the 3*d* electrons *the least***

In a many-electron atom, for a given principle quantum number ('n'), Zeff decreases with increasing 'l'

The energy of an electron depends on Z_{eff}

- **Because Z_{eff} is larger for 3*s* electrons (in the above n=3 example) they have a *lower energy* than 3*p* electrons (which in turn have *lower energy* than 3*d* electrons)**

In a many-electron atom, for a given principle quantum number ('n'), the energy level of an orbital increases with increasing 'l'

Electron spin and the Pauli exclusion principle

- **What determines the orbitals in which the electrons reside?**
- **How do the electrons populate the available orbitals?**

It was proposed (Uhlenbeck and Goudsmit, 1925) that electrons have yet another quantum property called *electron spin:*

- **A new quantum number for the electron called *the electron spin quantum number*, or m_s**
- **m_s has a value of +1/2 or -1/2**
- **The electron spin quantum number characterized the "direction of spin" of the electron**
    - **A spinning charge *produces a magnetic field***
    - **The opposite spins produce *opposite magnetic fields* which results in the splitting of the line spectrum into two closely spaced lines**

<u>Electron spin is crucial for understanding the electron structures of atoms:</u>

- **The *Pauli exclusion principle* (Wolfgang Pauli, 1925) states that *no two electrons in an atom can have the same set of four quantum numbers* (n, l, m_l and m_s)**
- **For a given orbital (e.g. $2p_z$) the values of n, l and m_l are *fixed*. Thus, if we want to put more than one electron into an orbital we must assign unique values to the magnetic spin (m_s quantum number)**
- **the m_s quantum number can only have two values (+1/2, and -1/2) therefore, *only two electrons at most can occupy the same orbital, and they have opposite values for magnetic spin***

What are the consequences of magnetic spin quantum number and the Pauli exclusion principle?

- **If we know the number of electrons in an atom we can assign probable quantum numbers and know something about their orbital shapes**
- **Provides an understanding for the periodic nature of the elements .**
